Radiopaque Copolymers of Styryldiphenylbismuth Vinylbenzylphosphonate and Methyl Methacrylate

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Styryldiphenylbismuth (SDB) has been copolymerized with vinylbenzylphosphonate ester (VBP) and methyl methacrylate (MMA) producing highly radiopaque copolymers and terpolymers. The phosphoryl ester groups were also converted to phosphonic acids and the polymers were characterized. Thermal analysis of the co- and terpolymers yielded single glass transition temperatures in the range 60−100 °C. Poly(styryldiphenylbismuth vinylbenzylphosphonate ester) copolymer is thermally stable up to 255 °C and degrades at ca. 285 °C, producing bismuth crystallites within the partially degraded polymer matrix. Radiopacities of the polymers were compared to aluminum standards and were found to be proportional to the bismuth contents. It was found that ca. 16 mol % (or 31.6 wt %) of styryldiphenylbismuth in the terpolymer of SDB, VBP, and MMA has double the radiopacity of aluminum.

Introduction

During the past two decades, considerable research effort has been devoted to the development of radiopaque polymers for medical applications[1−3] particularly because such materials can be analyzed in vivo by radiography, which is a nondestructive, analytical tool. Several reports from this and other laboratories have been published[4−11] in which radiopacifying agents were chelated with functional polymers, yielding homogeneous single phase X-ray contrast material. For example, copolymers of methyl methacrylate and glyme methacrylate,[4,5] containing an average of 22 ethylene oxide units, were synthesized and chelated with barium bromide dihydrate. Similarly, bismuth compounds[6−9] (Ph$_3$Bi, BiCl$_3$, and BiBr$_3$) and uranyl nitrate hexahydrate [UO$_2$(NO$_3$)$_2$·6H$_2$O] were dissolved in monomers containing carbonyl and phosphoryl groups.[10,11] Subsequent polymerization yielded transparent, homogeneous, radiopaque materials. Most of the heavy metal salts, which are miscible with functional polymers, are also susceptible to the presence of aqueous solutions. Excessive sorption of water in these materials often results in phase separation and loss of transparency. To avoid heterogeneity, leaching out and loss of radio-

pacities with time, monomers and polymers containing covalently linked heavy metals, such as styryldiphenylbismuth (SDB)[12−14] and α-methylstyryldiphenylbismuth, were synthesized in this laboratory. These are hydrophobic polymers that lack a proper hydrophobic/hydrophilic balance, properties that are required, for example, in medical implants.[15] This prompted us to copolymerize SDB with vinylbenzylphosphonate ester (VBP). This phosphonate ester can also mediate a strong bond between the copolymer and glass, hard tissues (e.g., dental enamel), and other resin components.[16] In the present manuscript, the copolymerizations of styryldiphenylbismuth with vinylbenzylphosphonate ester and methyl methacrylate and, subsequently, the hydrolysis of the phosphoryl ester into phosphonic acid in the copolymer were studied. The thermal property and radiopacity of the polymers were characterized, and a correlation between the molar concentration of the radiopacifying agent and the radiopacity of the polymers was established.

Experimental Section

Materials. Bismuth trichloride, bromotrimethylsilane, and *p*-bromostyrene were obtained from Aldrich Chemical Co. and used without further purification.

Azobisisobutyronitrile (AIBN) and benzoylperoxide (BPO) (Alfa Products) were recrystallized from a chloroform−methanol mixture before use. All solvents were obtained from Fisher Chemical Co. and used without further purification.

Methyl methacrylate was distilled before use at 35 °C/60 mmHg. Triethyl phosphite (Aldrich) was dried over calcium chloride and distilled before use at 45 °C/8 mmHg. Triphenylbismuth (Alfa Division of Morton Thiokol, Inc.) was used

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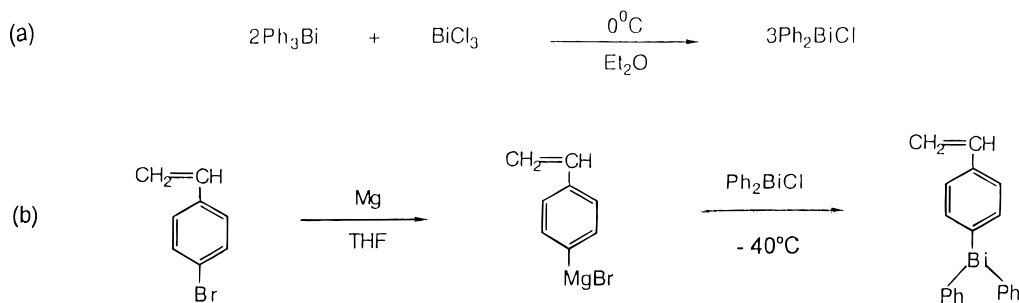(13) Ignatious, F.; Sein, A.; Delaviz, Y.; Cabasso, I.; Smid, J. *Polymer* **1992,** *33* (8), 1724.
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Scheme 1

(a)

$$2Ph_3Bi + BiCl_3 \xrightarrow[Et_2O]{0^0C} 3Ph_2BiCl$$

(b)

as received. Vinylbenzyl chloride, a mixture of meta and para isomers (7:3), was received through the courtesy of Dow Chemical Co. and distilled before use (50 °C/0.5 mmHg).

Note that all the halogen compounds are active and are poisonous if swallowed, especially bismuth trichloride, which is soluble in water. However, all these materials have high molecular weight and, therefore, have very low vapor pressure. Triphenylbismuth and styryldiphenylbismuth monomers and polymers are not considered toxic and are being developed presently to be used in medical implants.

Measurements. ^{1}H NMR spectra were recorded on a Bruker 300 MHz spectrometer using $CDCl_3$ and DMSO-d_6 as solvents. Mass spectral analysis was conducted on a Finnegan automated gas chromatography−mass spectrometer. Infrared spectra were recorded on a Nicolet Magna 750 FTIR spectrometer. The samples were cast from acetone solution on NaCl plates and were subsequently dried with an infrared lamp. The polymers molecular weights were determined relative to polystyrene standards using a GPC (Waters Associate Unit 590). The monomer SDB was analyzed on a Waters Associates HPLC Unit 6000 equipped with a reverse phase column. Acetonitrile was used as a solvent. Glass transition temperatures were obtained by differential scanning calorimetry, using a Perkin-Elmer DSC-4. All measurements were conducted at a scanning rate of 20 °C under a flow of nitrogen. Thermal gravimetric analysis was conducted on a V5.1A DuPont 2100 TGA. Transmission electron microscopy (JEOL JEM-2000EX) at 120 keV was used to determine the microstructure of the polymers.

Radiographic analysis was carried out with a Pickner condenser discharge mobile X-ray diagnostic unit model 1010 operating at 90 kV and 6 mA. Polymer pellets of 2 mm thicknesses were made in an infrared pellet press at 15 000 psi. Images were recorded on Kodak ultraspeed double-sided dental X-ray film Number DF-49.

The ion charge density determination of the phosphonic polymers was conducted using standard procedures.[17]

Syntheses. *Diphenylbismuth Chloride.* This compound was synthesized by reacting triphenylbismuth with bismuth trichloride in anhydrous diethyl ether according to a reported procedure.[18] The reaction mixture yields a white powdery solid with a sharp melting point at 186 °C.

Styryldiphenylbismuth (SDB). This compound was synthesized, with some modifications, according to a reported procedure and described in detail in an earlier reference.[13,19] Briefly, a 100 mL three-neck round-bottom flask fitted with a magnetic stirrer, reflux condenser, and addition funnel was charged with magnesium turnings (1.2 g, 0.05 mol) and tetrahydrofuran 15 mL. The addition funnel contained *p*-bromostyrene (9.1 g, 0.05 mol) dissolved in 20 mL of tetrahydrofuran. This solution was added dropwise to the flask while stirring vigorously for 45 min at ambient temperature, ca. 25 °C. The reaction mixture was stirred for an additional 1 h and cooled to −40 °C, and 30 mL of tetrahydrofuran was added. Diphenylbismuth chloride (19.9 g, 0.06 mol) was added

to this mixture in small lots over a period of 2 h, and the contents were stirred for 2 h. The reaction was ended by adding a saturated aqueous solution of ammonium chloride (10 mL), and the contents were then filtered over calcite. The yellow liquid obtained was dried over sodium sulfate and, after filtration, the solvent was removed by rotary evaporator. The yellow viscous syrup was dissolved in petroleum ether to precipitate the polymer formed during the Grignard reaction. After filtration, the solvent was removed to recover the yellow monomer (55% yield; Scheme 1). This synthesis also yields triphenylbismuth (~30%) and bis[styrylphenylbismuth] (~5%) and tris[stryllbismuth] (~2%). Further detail concerning this procedure is discussed later. Mass: m/z 466 (M[+]), 389 (M[+]−C_6H_5), 363 (M[+]−C_6H_4 and −$CH=CH_2$), 286 (M[+]−C_6H_4, −C_6H_5, and −$CH=CH_2$), 209 (M[+]−2C_6H_5, −C_6H_4, and −$CH=CH_2$). ^{1}H NMR: δ 5.27 (d, 1H, $J = 11$ Hz, CH=CH_2 (cis)), δ 5.88 (1H, $J = 18$ Hz, C=CH_2 (trans)), δ 6.75 (dd, 1H, $J = 18, 11$ Hz, CH=CH$_2$), δ 7.29−7.82 (multi, 14H, aromatic H).

Vinylbenzylphosphonate Ester (VBP). The monomer VBP was prepared according to ref 20. Briefly, a 150 mL two-neck round-bottom flask fitted with a magnetic stirrer and reflux condenser (fitted with calcium chloride tube) and thermometer was charged with triethyl phosphite (60 mL, 0.5 mol), vinyl-benzyl chloride (15 mL, 0.1 mol), and 6-*tert*-butyl-2,4-dimeth-ylphenol (0.2 mL, 4.5×10^{-4} mol). The mixture was stirred at 90 °C for 72 h under nitrogen. The unreacted triethyl phosphite was distilled at 45 °C at 8 mmHg, and vinylbenzyl chloride was removed at 55 °C at 0.5 mmHg. VBP was obtained at 116−130 °C at 0.6 mmHg in 68% yield [conventional polymerization of VBP with benzoyl peroxide yields is very high, ~95% of soluble polymer]. ^{1}H NMR: δ 1.16 (t, 6H, $J = 7$ Hz, 2OCH$_2$CH_3), δ 3.14 (d, 2H, $J = 22$ Hz, P−CH_2-ϕ), δ 4.0 (d, 4H, $J = 7$ Hz, P−O−CH_2), δ 5.25 (d, 1H, $J = 11$ Hz, CH=CH_2 (cis)), δ 5.85 (1H, $J = 18$ Hz, C=CH_2 (trans)), δ 6.71 (dd, 1H, $J = 18, 11$ Hz, CH=CH$_2$), δ 7.32−7.44 (4H, aromatic H para), δ 7.44−7.60 (4H, aromatic H meta). IR: 1250 S (νP=O), 1030−1060 S (νP−O−Et), 970 S (νP−O−C).

Polymer Synthesis. *Homopolymerization of Styryldiphenylbismuth (SDB).* The initiator AIBN (0.5 wt % of the monomer) was added to a solution of styryldiphenylbismuth (2.0 g) in toluene (8.0 g). The solution was heated to 65 °C under nitrogen atmosphere for 15 h. The product was then precipitated in methanol, dissolved in methylene chloride, reprecipitated in methanol, and dried under vacuum at 21 °C. Maximum yield of 60−65% was achieved after 30 h. The $\bar{M}w$ of poly(styryldiphenylbismuth), which was polymerized at low conversion, was 11 000 (2.1 molecular weight distribution) with T_g of 106 °C.

Copolymerization of Styryldiphenylbismuth (SDB) and Vinylbenzylphosphonate Ester (VBP) [Scheme 2a]. In a typical preparation, an equimolar mixture of styryldiphenylbismuth (4.66 g) and vinylbenzylphosphonate ester (2.54 g) was dissolved in 10 mL of toluene. AIBN (0.5 wt % of monomers) was added and polymerization conducted under nitrogen atmosphere at 65 °C for 15 h. The polymer was precipitated with excess hexane, washed thoroughly, then redissolved in methylene chloride and precipitated into hexane. The product
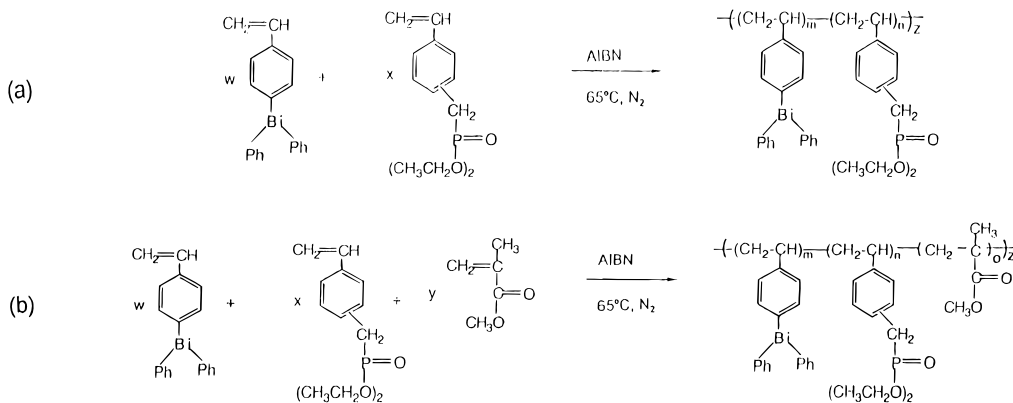
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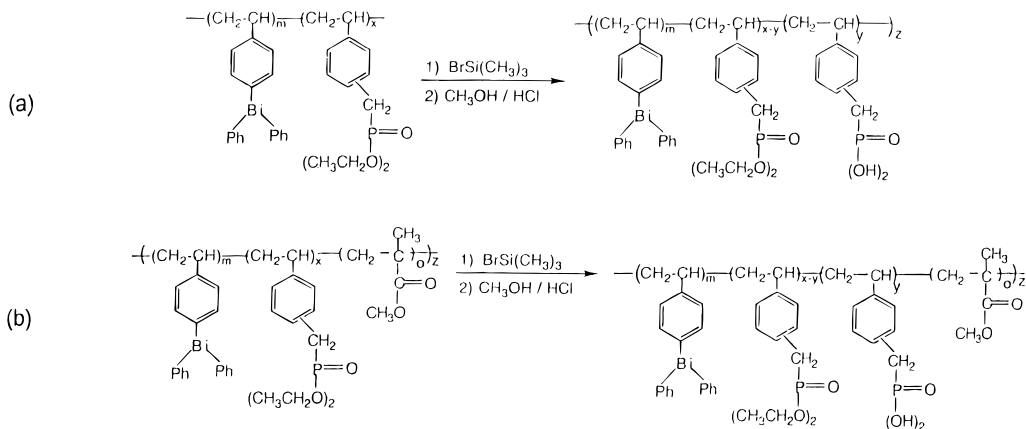
Scheme 2

Scheme 3

Table 1. Composition and Molecular Weight of Bismuth Polymers

	polymer compn[b] (mol %)				SDB[d]	bismuth[d]
designation[a]	SDB	VBP	MMA	MW[c]	(wt %)	(wt %)
B1	100	0	0	11 000	100	44.8
BP (1:1)	50	50	0	17 000	65	29.0
BPM22	22	44	34	21 000	41	18.6
BPM16	16	50	34	32 000	32	14.6

[a] Designations: B for styryldiphenylbismuth, P for vinylben-zylphosphonate ester, M for methyl methacrylate. The number represents the molar ratios of SDB, VBP, and MMA in copolymers. [b] Determined by ^{1}H NMR spectroscopy. [c] Calculated by gel permeation chromatography. [d] Weight % of SDB monomer and bismuth in polymers is based on repeat unit formula.

was eventually dried at ambient temperature to yield a glassy copolymer; $\bar{M}w$ and compositions are reported in Table 1.

Copolymerization of the Mixture Styryldiphenylbismuth (SDB), Methyl Methacrylate (MMA), and Vinylbenzylphosphonate Ester (VBP) [Scheme 2b]. An equimolar mixture of SDB, VBP, and MMA was polymerized under the same conditions delineated above. Fractions from the polymerization solution were collected after 15, 25, and 30 h. The copolymers were precipitated into hexane, redissolved in methylene chloride, collected in excess of hexane and dried at ambient temperature. The $\bar{M}w$ and compositions of the terpolymers were determined with GPC and ^{1}H NMR, respectively, as reported in Table 1.

Hydrolysis of Phosphoryl Ester to Phosphonic Acid in the Copolymers [Scheme 3]. The phosphoryl ester group was hydrolyzed to phosphonic acid in some of the copolymers and terpolymers. A specific method of hydrolysis[21,22] of $-PO(OR)_2$

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was used as follows. A quantity of 1.0 g of poly(VBP−SDB) copolymer, shown as BP (1:1) in Table 1 and 15 mL of methylene chloride was added to a 50 mL two-neck round-bottom flask fitted with a magnetic stirrer, reflux condenser, and addition funnel. To this, a solution of bromotrimethylsi-lane 1.0 g (6.4×10^{-3} mol) in 5 mL of methylene chloride was added dropwise while stirring vigorously for 15 min at 25 °C. Stirring was continued for an additional 1 h. The solvent and volatiles were then removed by rotary evaporator. The viscous oil obtained was dissolved in 10 mL of tetrahydrofuran. While being stirred, this solution was treated with 5 mL of 20% hydrochloric acid in methanol. After 1 h, the solution was poured into an excess of water in a Teflon beaker and the polymer was precipitated. The polymer was then washed in deionized water and dried at 25 °C in a vacuum oven to yield 90% (0.84 g) soluble polymer (Scheme 3a). The terpolymers were hydrolyzed by employing a similar procedure, as shown in Scheme 3b. The hydrolyzed products of PVBP are designated PVBPa.

The ion exchange density (ICD) for all phosphonic acid polymers was measured and found to be in the range 1−3 meq/g. Note that the monomer VBPa should have 10.1 meq/g. These hydrolyzed copolymers are soluble in polar solvents such as ethanol, formamide, and dimethyl sulfoxide.

Results and Discussion

Synthesis and Polymerization. Styryldiphenyl-bismuth (SDB) was synthesized according to Braun et al.[19] who also reported the reactivity ratios in the copolymerization of styrene with a series of diphenyl-styryl monomers of group VA elements (P, As, Sb, and Bi). As mentioned earlier, the monomer SDB was prepared by reacting the Grignard of *p*-bromostyrene with Ph$_2$BiCl. This yielded a complex mixture of triphenylbismuth, styryldiphenylbismuth (SDB), and its di- and tristyryl derivatives, as revealed by reverse

Table 2. Composition and Molecular Weight of Bismuth Polymers Containing Phosphonic Acid Derivatives

	polymer compn (mol %)		conversion to
designation[a]	VBPa	VBP	phosphonic acid[b] (%)
BPPa (5:1:4)	40.0	10.0	80
BPPaM22	36.0	8.0	81
BPPaM16	40.0	10.0	80

[a] Designations: B, styryldiphenylbismuth; P, vinylbenzylphosphonate ester; Pa, vinylbenzylphosphonic acid; M, methyl methacrylate. [b] Determined by ^{1}H NMR spectroscopy.

phase HPLC.[13] Organobismuth compounds are prone to redistribution reactions. Gilman and Yablunky[23] suggested that the organometallic salt, in general, showed the following equilibria:

$$R_2MX \rightleftharpoons RMX_2 \rightleftharpoons R_3M + MX_3 \qquad (1)$$

These authors also reported that synthesis of diphenyl-α-naphthylbismuth (from *p*-tolyl-α-naphthylbismuth via the Grignard reaction of bromonaphthlene) leads to higher yields when the reaction is carried out at 0 °C, compared to that at room temperature or at reflux. This could be due to a lower redistribution of R_2BiCl at low temperatures, which prompted us to conduct the SDB synthesis at −40 °C. This condition was found to give a better yield of styryldiphenylbismuth (55%) compared to what was earlier reported from this laboratory (42%).[13] Copolymerizing the monomer SDB with VBP and MMA in bulk polymerization produced some cross-linked products due to the presence of di- and tristyrylbismuth. To avoid cross-linking, the homopolymerization of SDB and its copolymerization with VBP and MMA were done at low conversions using toluene as the solvent (Table 1). Thus, a number of soluble polymers, with different compositions, were obtained from polymerization mixtures having different monomer ratios. The chemical composition of the copolymers was determined by ^{1}H NMR, comparing the proton of the $-CH_2O$ of the phosphonyl ester with protons of the aromatic ring. In the terpolymer, the methoxy groups of MMA were also compared. It is important to note here that the ^{1}H NMR spectra show residual vinyl protons, indicating that some di- and tristyrylbismuth were also incorporated into the polymer chain and could be the reason for cross-linking at high conversions. Thus, for example, solution polymerization for 30 h resulted in partial cross-linking of the terpolymer, which was insoluble after precipitation from hexane [designated in the text as BPM (ins)].

The co- and terpolymers of SDB−VBP−MMA were hydrolyzed by bromotrimethylsilane/methanol (Table 2). This method selectively hydrolyzes the phosphoryl ester to phosphonic acid, leaving carbonyl esters intact, as proven by FTIR spectroscopy and titration of the phosphonic acid. The results shown in Table 2 indicate that in these copolymers, 80−90 mol % of phosphoryl ester were converted to phosphonic acid.

Infrared spectroscopy was used for characterization of the hydrolysis of phosphonate esters to phosphonic acid. The poly(VBP−SDB) copolymer exhibits strong bands at 1245 cm^{-1} (P=O), 1030−1060 cm^{-1} (P−O−Et), and 970 cm^{-1} (P−O−C). Upon conversion to the phosphonic acid version, the polymer displays a very weak

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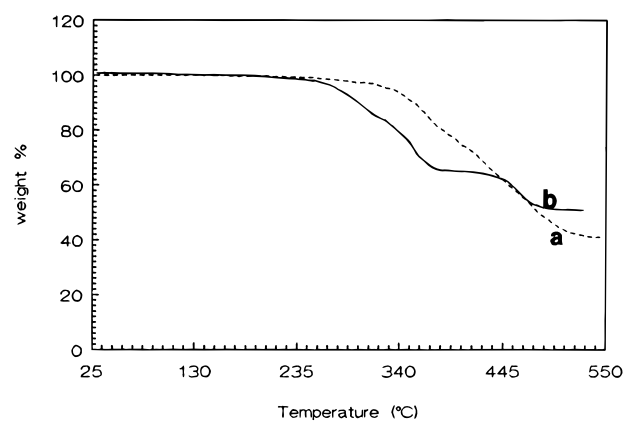

Figure 1. Thermal gravimetric analysis (TGA) of (a) poly(styryldiphenylbismuth) and (b) poly(benzylphosphonate diethyl ester−styryldiphenylbismuth, 1:1) copolymer.

peak at 1252 cm^{-1} and a strongly overlapping series of bands at 1040−940 cm^{-1}. This broad band area is due to inter- and intramolecular hydrogen bonding interactions between the phosphoryl group −P=O and −P(OH)$_2$. Since this hydrolysis is specific for the phosphoryl ester, the MMA units in the terpolymer remain intact after the reaction. Infrared spectra, however, clearly show that the stretching vibration band of C=O at 1727 cm^{-1} broadens and shifts to 1710 cm^{-1}, indicating interaction of the carbonyl with the phosphonic acid group.

Thermal Analysis and Microstructure Properties. Thermal degradation of the homopolymer (PSDB) and poly(SDB−VBP) copolymer was conducted over the temperature range 25−500 °C at a scanning rate of 20 °C/min under nitrogen atmosphere (Figure 1). The homopolymer (Figure 1a) shows a steep degradation curve at 330−390 °C with a weight loss of 28%. The final degradation of 27% in the temperature range 390−490 °C resulted in a black residue of 43%, which is close to the theoretical amount of bismuth in the homopolymer. Degradation initiating at ca. 300 °C is due to the cleavage of the bismuth−phenyl bond, as can be confirmed from differential scanning calorimetry, which shows the release of bismuth metal as discussed below. This bond is relatively weak, with a bond dissociation energy of 46.2 kcal/mol in triphenylbismuth.[24] The decomposition recorded at 390−490 °C can be attributed to the degradation of the polystyrene backbone, resulting in low molecular weight products.[25] Thermogravimetric analysis of the copolymer (Figure 1b) shows a weight loss of 33% in the temperature range 255−370 °C, and 14% at 370−485 °C, resulting in a black residue of ∼50%. Weight loss at 255 °C is due to cleavage of the diphenyl bond and ethyl ester of the VBP moiety in the poly(VBP−SDB) copolymer. Cabasso et al.[26] reported that the thermal degradation of PVBP at 340−350 °C is due to the loss of the ethyl ester group leading to the highly cross-linked network, resulting in the stability that the matrix exhibits between 370 and 450 °C. The high amount of char is due to the contribution of phosphorus oxide residue.[26,27]

Glass transition temperatures of poly(VBP−SDB) copolymers and their phosphonic acid versions were

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Table 3. Glass Transition Temperature of Bismuth Polymers and Their Phosphonic Acid Derivatives

designation[a]	polymer compn[b] (mol %)				$T_g{}^c$ (°C)		ΔC_p
	SDB	VBP	VBPa	MMA	onset	midpoint	cal g^{-1} deg^{-1} × 10²
B1	100	0	0	0	91.0	106.0	1.6
BP (1:1)	50	50	0	0	73.5	78.0	2.2
BPM22	22	44	0	34	65.0	68.0	3.2
BPM16	16	50	0	34	66.0	70.0	4.1
BPPa50	50	10	40	0	83.0	96.0	3.8
BPPaM22	22	8	36	34	78.0	83.5	3.1
BPPaM16	16	10	40	34	77.0	82.0	2.7

[a] Designations: B, styryldiphenylbismuth; P, vinylbenzylphosphonate ester; Pa, vinylbenzylphosphoric acid in hydrolyzed polymers; M, methyl methacrylate. [b] Determined by ¹H NMR spectroscopy. [c] Calculated from differential scanning calorimetry.
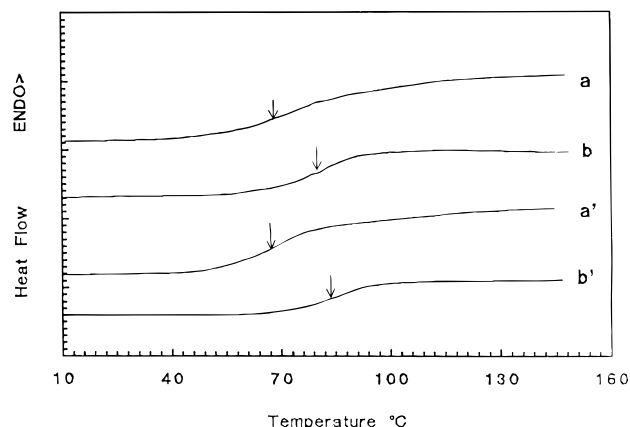
Figure 2. Differential scanning calorimetry (DSC) traces of the terpolymers poly(SDB–VBP–MMA) and their hydrolysis products BPPaM: (a) BPM22; (a′) BPM16; (b) BPPaM22; (b′) BPPaM16.
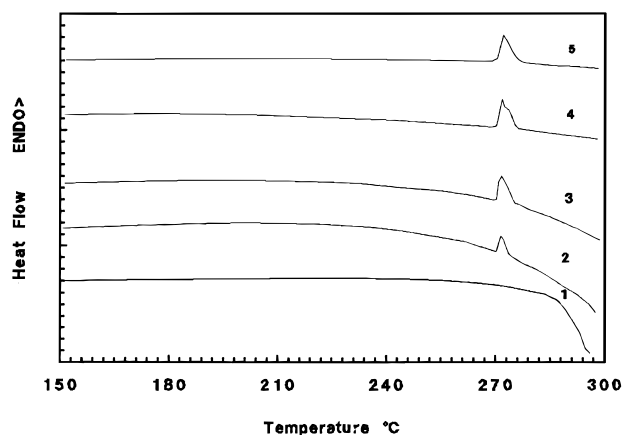

Figure 3. Differential scanning calorimetry traces of poly-(VBP–SDB, 1:1) copolymers showing (curve 1) first scan with a degradation point at ca. 285 °C, and (curves 2–5) four consecutive scans showing the development of the crystalline melting endotherm of bismuth in the partially degraded polymer.

further characterized by differential scanning calorimetry. Before measurements, each polymer was annealed at 80 °C for 10 min and then scanned three times. The T_g was determined from the second scan (Figure 2, Table 3). The T_g of the homopolymer previously reported are 110 °C for PSDB,[9] 9 °C for PVBP,[28] and 108–115 °C for PMMA. All the polymers shown in Table 3 are amorphous, displaying a single T_g. The phosphonate acid derivatives exhibit a higher T_g than the ester

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Table 4. Electrical Resistivity of Bismuth Polymers

designation[a]	polymer compn (mol %)			electrical resistivity at 100 kHz (kΩ cm)	
	SDB	VBP	MMA	pure	degraded[b]
B1	100	0	0	4.8	2.27 × 10^{-3}
BP (1:1)	50	50	0	4.96	1.70 × 10^{-1}
BPM22	22	44	34	4.90	12.4 × 10^{-1}

[a] Designations: B, styryldiphenylbismuth; P, vinylbenzylphosphonate diethyl ester; M, methyl methacrylate. [b] Polymer samples were scanned in DSC from 50 to 300 °C, and electrical resistivity is measured after third scan.
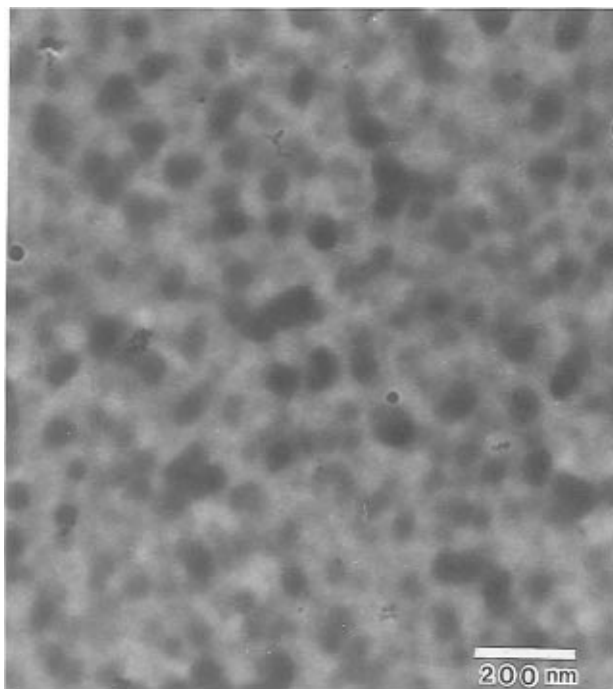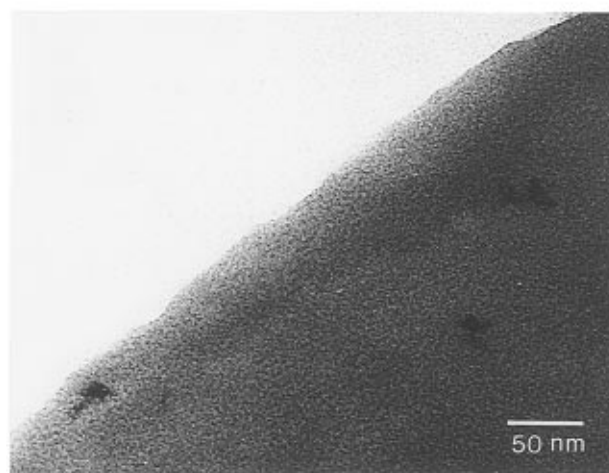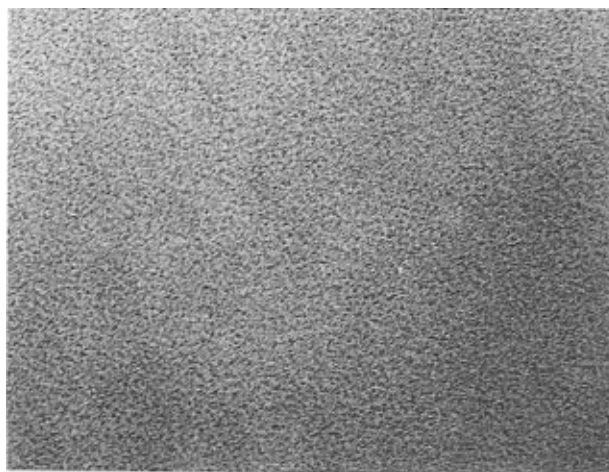

Figure 4. Transmission electron micrograph of poly(vinyl-benzylphosphonate ester–styryldiphenylbismuth, 1:1) copolymer. The black–gray diffused domains of the bismuth moieties are 5–60 nm in size.

derivative, as expected. The transition is broadened due to inter- and intra-hydrogen bonding of the phosphonic acid. A higher value of ΔC_p (3.80 cal/g deg) was also obtained for the phosphonate acid version, as compared to the parent copolymer ($\Delta C_p = 2.2$ cal/g deg).

A series of DSC scans of the copolymer that were taken up to 300 °C (Figure 3) show that after the initial decomposition (scan 1) an endotherm at 271 °C, coinciding with the melting of bismuth metal, appears at the second scan. The formation of bismuth metal lowers the electrical resistance of these partially degraded copolymers, as shown in Table 4. All the degraded samples show much lower electrical resistivity than original polymers at an ac of 100 kHz. For comparison,

Figure 5. Two transmission electron micrographs of partially degraded poly(vinylbenzyl phosphonate ester−styryldiphenyl-bismuth, 1:1) copolymers. This sample was heated in a DSC pan to 300 °C (trace 3 in Figure 5). The micrographs show a well-dispersed black domain of bismuth 4 ± 1 nm in size.

the resistivity of pure bismuth at 0 °C is 106 mΩ cm.[30]

These polymers were further studied by transmission electron microscopy. Ultrathin samples of the copolymer were prepared by casting onto film on a TEM grid or were microtomed into 50 nm sections. The bismuth has sufficient contrast, and a staining agent was not required. This can be seen by comparing the TEM micrographs of poly(VBP−SDB, 1:1) copolymer and its partially degraded version that was taken from scan 3 (Figure 3). The TEM micrograph of the copolymers (Figure 4) shows a random distribution of the bismuth moieties displaying diffused domains in the range 5−60 nm. This copolymer has a single T_g of 78 °C (Table 3). The TEM micrographs of the partially degraded copolymer (Figure 5) show a more uniform bismuth dispersion of molecular and crystalline grains of ∼4 nm; no T_g could be detected. The TEM micrograph of poly(styryldiphenylbismuth), which is not shown here, is uniformly black when compared to the gray hue of the copolymer in Figure 4.

Radiopaque Properties. Several positive radiographs of PSDB, poly(VBP−SDB) copolymer, and ter-
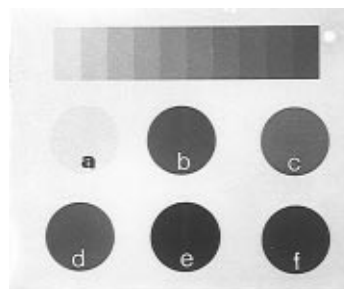

Figure 6. Positive radiographs of radiopaque polymers (see Table 1) measured against aluminum stepwedge bar with steps from 0.5 to 5 mm: (a) PMMA/2.2; (b) BPM30/2.1; (c) BPM16/1.9; (d) BPM22/1.9; (e) BP50/2.0; (f) B100/1.9.
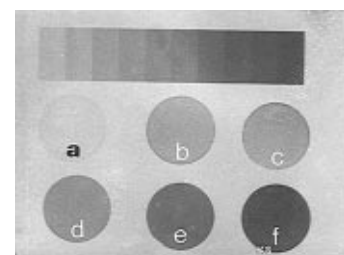

Figure 7. Positive radiographs of terpolymer BPM16 measured against aluminum stepwedge bar with steps from 0.5 to 5 mm. Sample designations in mol % SDB/thickness (mm) are (a) PMMA/2.20, (b) BPM16/0.58, (c) BPM16/0.76, (d) BPM16/0.92, (e) BPM16/1.36, and (f) BPM16/2.06.

polymer poly(SDB−VBP−MMA) were measured against an aluminum stepwedge and a PMMA sample, as shown in Figure 6. The comparison of the radiopaque materials with an aluminum stepwedge allows the radiopacity to be expressed in millimeters of aluminum, a standard that is frequently used for X-ray contrast in plastics technology and in medical applications.[31] The observed contrast is determined by the thickness of the specimen in the direction of the X-ray beam and by the concentration of the radiopacifying materials. All the specimens in Figure 6 are ca. 2 mm and show a higher radiopacity compared to an aluminum stepwedge of equivalent thickness. Figure 7 shows that terpolymer samples of varied thicknesses of BPM16 provide different radiopacities. A linear correlation exists between the radiopacity and the thickness of a specimen of a constant concentration radiopacifying material. Thus, a 0.98 mm thick pellet of this BPM16 provides the radiopacity equivalent to 2 mm of aluminum (Figure 8).

In a separate measurement, known quantities of terpolymer BPM16 were dissolved in MMA monomer and the solutions were polymerized at 65 °C for 48 h. Subsequently, the polymer blends were cut into 2 mm pellets and the radiopacity was measured (Figure 9). The radiopacity R [expressed in millimeters of polymer per millimeter of the aluminum] and the molar concentration $[M_a]$ of the radiopacifier were found to be related by the following expression:[32]

$$R = R_0 + (R_0 - R_a)\bar{V}_a M_a \qquad (2)$$

where R_0 and R_a are the respective radiopacities of the

(29) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic Press: New York, 1971.

(30) *Handbook of Chemistry and Physics*, 67th ed.; CRC Press: Boca Raton, FL, 1986; p F-120.

(31) *Radiopacity of Plastic for Medical Use*; American National Standards Institute/American Society for Testing of Materials Standard; ANSI/ASTM; p F640−79, Method C.

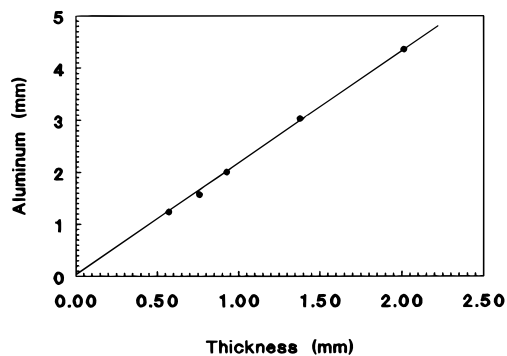(32) Cabasso, I.; Smid, J. *Bull. Bismuth Inst. (Brussels)* **1990**, *60*, 1.

Figure 8. Radiopacities in millimeter of aluminum of the terpolymer BPM16 as a function of thickness of the pellet.
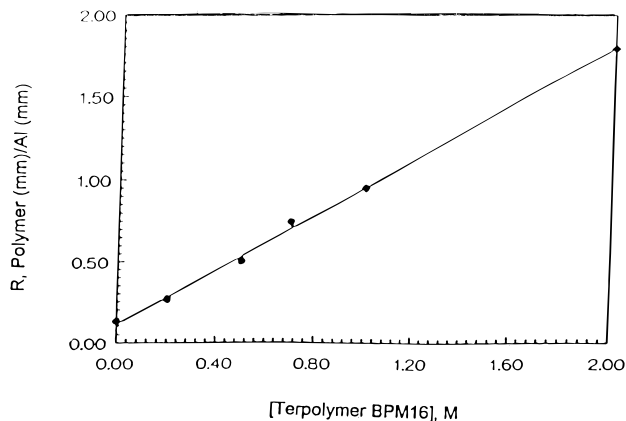

Figure 9. Plots of radiopacity R of polymer blend (PMMA/terpolymer−BPM16) measured in mm aluminum *vs the* molar concentration of the terpolymer (see Table 1 for identification).

pure polymer (i.e., PMMA) and additive, and $\bar{V}_a$ is the molar volume of the additives. This relationship was observed experimentally for bismuth trihalide[8] in PMMA and Ph₃Bi solubilized in different polymers.[9] From Figure 9, the molar concentration M_a, or wt %, of terpolymer at which the radiopacity would be equal to that of aluminum can be determined. This M_a value for the terpolymer used in Figure 9 is 1.05 M (61.6 wt %) in MMA.

Conclusions

A homopolymer and co- and terpolymers of styryldiphenylbismuth with vinylbenzylphosphonate ester and methyl methacrylate were prepared successfully, yielding materials with radiopacity exceeding the equivalent thickness of aluminum. The phosphoryl ester groups in these polymers were converted to phosphonic acid derivatives and, thus, can further increase radiopacity through strong chelation with heavy metal salts.[11] The phosphonate moieties impart good adhesive and mechanical properties.[16] When copolymerized with rigid bismuth monomers, they maintain good thermal properties. The fact that only one glass transition temperature is found in the co- and terpolymers is significant; this calls for the determination of the copolymerization reactivity ratios of styryldiphenylbismuth with the VBP and MMA. It was recently found that the last two have close copolymerization ratios.[16] The nature of the crystalline bismuth in the partially degraded polymers also has to be studied further. This may lead to a host of useful solid-state properties (e.g., semiconductivity) if indeed the small crystallites are being generated in nanoscale dispersions (Figure 5). Further work is being conducted in this laboratory with an aim toward application of these polymers as radiopaque adhesives. Also, synthetic studies aimed at obtaining a pure styryldiphenylbismuth monomer, without the di- and triphenylbismuth derivatives, are currently being conducted.